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[Second Edition.]



PATENT SPECIFICATION

587,378

Application Date: Dec. 4, 1944. No. 24172/44.

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(One Complete Specification-left (under Section 16 of the Patents and Designs Acts, 1907 to 1942): Dec. 2, 1945.

Specification Accepted: April 23, 1947.

PROVISIONAL SPECIFICATION

No. 24172 A.D. 1944

Improvements in or relating to the Manufacture of Ethylene.

We, EDWARD HUNTER, CHARLES GEORGE PAULIN FRACHEM and RAYMOND BLISS RICHARDS, all of Winnington Hall, Northwich, Cheshire, and all British Subjects, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention to be as follows:-

This invention relates to the manufacture of ethylene under high pressure by dehydration of ethanol:

It is known that ethanol can be catalytically dehydrated to give ethylene. One process involves passing ethanol vapour over catalysts such as alumina, or phosphoric acid suspended on coke, at a temperature of 300°-400° C. Other processes involve heating ethanol with concentrated sulphuric or phosphoric acid. Such processes are only known to operate at or near atmospheric pressure, and when ethylene is required under pressure it must then be compressed. Compressed ethylene is required for storage in cylinders, and also for carrying out many chemical reactions, in particular polymerisation to give solid or liquid products.

We have now found that ethylene can be prepared directly under pressure at suitably high temperatures by catalytic dehydration of ethanol under whatever pressure is required.

According to the present invention, we manufacture ethylene at a high pressure by subjecting ethanol at a high pressure and temperature to contact with a dehydration catalyst, and if desired separating the ethylene produced from unconverted ethanol and undesired by-products.

The process may be carried out at pressure above 50 atmospheres, generally at pressures such as 250-1500 atmospheres or higher. Suitable temperatures are generally above 200° C. and preferably between 250° and 450° C. At temperatures below 250° C. only a minor

fraction of the ethanol is converted. As dehydration catalyst we may employ phosphoric acid, concentrated sulphuric acid, gamma alumina, caustic soda, and other catalysts preferably acid catalysts known for the dehydration of ethanol at atmospheric pressure. The time of contact required depends *inter alia* on the pressure, temperature, catalyst, and the required degree of conversion of the ethanol, a time between 10 seconds and 3 minutes is generally sufficient, but longer times up to 1 hour and more may be used.

Unconverted ethanol and undesired by-products can be separated without reducing the pressure of the ethylene, by methods known for separating these substances from crude ethylene at atmospheric pressure. Such methods include cooling, preferably at constant pressure, followed by scrubbing with warm water which may contain alkali to remove any acid catalyst present in the ethylene; and adsorption on active charcoal. The ethylene obtained is however sufficiently pure for some purposes when the water of dehydration is removed by condensation.

EXAMPLE.

The apparatus used consists of a vertical glass tube closed at the top end, filled with and having the bottom end immersed in mercury, the tube and mercury being wholly enclosed within a pressure vessel. 1 part by weight of ethanol and 0.05 part by weight of phosphoric acid are introduced into the tube, and occupy one-four hundredth of the tube volume. The pressure vessel is closed and the pressure is raised to 1000 atmospheres by pumping in oil. The temperature is then raised to 350° C. for 1 hour while maintaining the pressure at 1000 atmospheres, after which the vessel is cooled. The tube is found to be practically full of ethylene.

Dated the 4th day of December, 1944.

E. A. BINGEN,
Solicitor for the Applicants.

PROVISIONAL SPECIFICATION

No. 24173 A.D. 1944.

Improvements in or relating to the Manufacture of Ethylene
Polymers.

We, EDWARD HUNTER, CHARLES GEORGE PAULIN FRASCHER and RAYMOND BLISS RICHARD, all of Winnington Hall, Northwich, Cheshire, and all British Subjects, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, to hereby declare the nature of this invention to be as follows:—

This invention relates to the manufacture of ethylene polymers under high pressure from ethanol.

It is known that ethanol can be catalytically dehydrated to give ethylene, and that ethylene can be converted into polymers and interpolymers by processes carried out at elevated pressures. The manufacture of solid and semi-solid polymers and high molecular weight interpolymers of ethylene by such processes is described in Specifications 471,590, 497,643 and in Applications 8070/40 and 4729/41. Liquid polymers of ethylene may also be prepared by processes which involve elevated pressures. In all these processes a considerable amount of gas compression is required.

The objects of this invention are to dispense with the need for most or all of the gas compression hitherto involved in high pressure processes for the polymerisation of ethylene, and to simplify the production of ethylene polymers from ethanol.

According to the present invention, we manufacture substances having recurring $-C_2H_4-$ units by a process which comprises dehydrating ethanol at a high pressure and temperature, and subjecting at least part of the material so obtained to ethylene polymerisation conditions.

A process for the dehydration of ethanol at a high pressure and temperature is described in co-pending Application 24172/44. In that process, ethanol is subjected to contact with a dehydration catalyst such as phosphoric acid at a high pressure generally 250—1500 atmospheres, and a high temperature generally 250°—450° C. If desired, unconverted ethanol and undesired by-products may be separated from the crude ethylene, e.g., by cooling at constant pressure followed by scrubbing with warm water. The polymerisation conditions involve an elevated temperature and pressure, and if desired a polymerisa-

tion catalyst such as oxygen or a peroxide compound, and if desired an aqueous or other liquid medium. There may also be present other substances which form interpolymers or telomers with olefines.

In one aspect of the present invention we carry out the process in three stages. The first stage is the high pressure dehydration of ethanol, the second stage is the removal of unwanted materials from the dehydration products, and the third stage is the subjecting of the purified dehydration product to ethylene polymerisation conditions. Such stages may in fact be successive parts of a continuous flow process. In cases where no purification of the crude dehydration products is needed, the dehydration and polymerisation may be carried out simultaneously in a single plant unit. It is advantageous to maintain the same pressure for the whole process, but if desired, when working the dehydration and polymerisation steps separately, the pressure may be raised or lowered between the two steps. For example, the dehydration may be carried out at 200 atmospheres and the polymerisation at 1000 atmospheres, so that the bulk but not all of the compression required in the known processes is avoided.

The method of carrying out the above invention is illustrated by the following typical description, in which the quantities and conditions employed are not critical.

We pump ethanol at a pressure of 1000 atmospheres, containing 0.05 parts of phosphoric acid per part of ethanol, through a tubular reaction vessel maintained at 350° C., the rate of pumping being adjusted so that the ethanol takes two minutes to pass through the heated zone. The product issuing from this tube is predominantly ethylene and water, but may also contain some unchanged ethanol or phosphoric acid and by-products of the dehydration such as ether. This mixture passes into a second vessel maintained at 45° C., through which liquid water, which may be mildly alkaline, is pumped, 10 parts by weight of water being used per part of ethanol dehydrated. The water removes the bulk of the unchanged ethanol, phosphoric acid and ether, and is drawn away from the bottom of the vessel. The scrubbed ethylene, still at 1000 atmospheres pressure, passes into a

third vessel maintained at 180° C. in which polymerisation occurs. Oxygen, the catalyst for the polymerisation, is injected at a point between the second and third vessel, at a rate equivalent to about 50—200 parts per million parts of ethylene. The product of polymerisa-

tion is extracted from the polymerisation vessel and separated into gaseous ethylene and solid ethylene polymer.

Dated the 4th day of December, 1944.

E. A. BINGEN,

Solicitor for the Applicants.

COMPLETE SPECIFICATION.

Improvements in or relating to the Manufacture of Ethylene and Ethylene Polymers.

We, EDWARD HUNTER, CHARLES GEORGE PAULIN FEACHEM and RAYMOND BLISS RICHARDS, all of Winnington Hall, Northwich, Cheshire, and all British Subjects, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the manufacture of ethylene from ethanol and to the manufacture of polymerisation products containing recurring $-C_2H_4-$ groups.

It is known that ethylene can be polymerised at very high pressures to yield solid and semi-solid products by the process described and claimed in Specification No. 471,590. High molecular weight interpolymers can also be obtained from ethylene with other organic compounds containing one or more carbon-carbon double bonds and capable of forming polymers by a similar process, as described in Specification No. 497,643. Moreover, these reactions can be carried out in the presence of an aqueous medium as described in Application No. 8070/40 (as open to public inspection under Section 91(4), and claimed in Application No. 4729/41 (Specification No. 578,584). Liquid polymers of ethylene may also be prepared by processes which involve elevated pressures. In all these processes a considerable amount of gas compression is required.

For economic reasons it is frequently advantageous to employ ethanol and dehydrate it as the source of ethylene in the above processes. The known processes of making ethylene from ethanol involve subjecting it to an elevated temperature, generally 300°—400° C., in presence of a dehydration catalyst such as activated alumina, or phosphoric acid which may be suspended on coke or other inert porous material. These processes are

generally operated at atmospheric pressure, but reduced or elevated pressure may be used as shown in Specification 317,500. It is also known that ethylene and water recombine to give ethanol in presence of such catalysts at lower temperatures, e.g., 100°—250° C., either at atmospheric or at elevated pressures such as 10—100 atmospheres.

The objects of this invention are to dispense with the need for most or all of the gas compression hitherto involved in the preparation of compressed ethylene, and to simplify the production of ethylene polymers from ethanol.

According to the present invention, we manufacture ethylene directly under pressure by a process which comprises subjecting ethanol to contact with a dehydration catalyst at an elevated pressure between 350 and 1500 atmospheres, and a high temperature, preferably 300°—600° C. If desired, unconverted ethanol and undesired by-products may be separated from the crude ethylene without considerable reduction of pressure, e.g., by cooling at constant pressure and/or scrubbing with warm water.

According to a further feature of this invention, we manufacture polymerisation products having recurring $-C_2H_4-$ groups by a process which comprises contacting the product so obtained with an ethylene polymerisation catalyst while still at an elevated temperature and pressure.

The ethanol dehydration is carried out at a temperature exceeding 200° C., preferably at 300°—600° C. These high temperatures favour the production of ethylene rather than other dehydration or decomposition products. The dehydration does not occur in the absence of dehydration catalysts, which materials include acid catalysts such as phosphoric acid either mixed with the ethanol or suspended on an inert porous material such as coke or pumice, cadmium phosphate, and inorganic catalysts such as

alumina and activated clays. The amount of catalyst required depends *inter alia* upon the catalyst used, the temperature and pressure, the time allowed, and also upon the fraction of the ethanol to be dehydrated. For phosphoric acid we prefer to have at least 1% of H_3PO_4 present based on the weight of ethanol, and generally 5–10% is employed. For alumina, we prefer to employ at least one part by weight per 2 parts of ethanol in the catalyst vessel. At a temperature of 300°–450° C. the time of contact of the ethanol with the catalyst should exceed two minutes and is preferably at least 10 minutes. Slightly shorter times of contact are permissible at temperatures of 450°–600° C. and these temperatures are preferred whenever they can be used in the equipment available. For high conversions, however, longer times such as 5 hours are advantageous. Such conditions generally give about 20–30% dehydration of ethanol to ethylene, the proportion depending upon the catalyst, temperature and time of contact, and the pressure used.

The polymerisation is carried out in presence of an ethylene polymerisation catalyst. Such catalysts include oxygen; peroxides such as hydrogen peroxide, alkyl and acyl peroxides and alkyl hydroperoxides; per-acids and their salts such as persuccinic acid, alkali persulphates, percarbonates and perborates; amine oxide; hydrazine; oximes; and organometallic compounds such as lithium butyl. In the case of oxygen, the amount used is generally between 5 and 2000 parts by weight per million parts of ethylene present, and in the case of other catalysts the amount used is generally between 0.01 and 1% of the weight of ethylene present.

The temperature and pressure required for the polymerisation depend *inter alia* on the catalyst used, the proportion of ethylene in the ethanol dehydration product employed, and the product required. For oxygen catalyst the temperature is greater than 100° C. and is generally between 150° and 400° C., and the pressure is greater than 500 atmospheres and is generally above 800 and less than 2000 atmospheres, when making solid polymers. For other catalysts, particularly per-compounds such as a persulphate, the temperature is preferably between 60° and 150° C., and the pressure is greater than 50 atmospheres and is preferably between 70 and 1000 atmospheres.

When carrying out both dehydration and polymerisation, it is clearly advantageous to use the same pressure for both operations. Generally some cooling of

the dehydration products is required in order to bring them to the optimum conditions for polymerisation, and such cooling is advantageously carried out at constant pressure. In a batch operation this may be done by injecting an inert liquid material such as oil during the cooling, but in a continuous flow process no such injection is needed as the pressure automatically remains substantially constant. High pressures are generally required for the polymerisation, but too high pressures such as 2000 atmospheres and higher are difficult to use commercially and do not favour the dehydration of ethanol to ethylene and are therefore undesirable. We therefore prefer to carry out the whole process at a pressure between 350 and 1000 atmospheres.

If cooling is carried out between dehydration and polymerisation in order that the optimum temperatures of dehydration and polymerisation can both be used, partial recombination can occur unless the crude ethylene is separated from the dehydration catalyst. With solid catalysts such as alumina, the products are preferably physically separated from the catalysts before cooling, for example as in a continuous flow process. With fluid catalysts such as phosphoric acid or its unstable compounds, the products are preferably separated by chemical methods such as by contacting with an aqueous solution of alkali while at the elevated pressure. Alternatively, the cooling can be effected rapidly, especially when a relatively low temperature such as 60°–100° C. is being employed for the polymerisation, because under these conditions the dehydration products are rapidly brought down to a temperature at which the rate of recombination is negligible. Cooling also can remove appreciable proportions of by-products and unchanged ethanol from the dehydration products and thus enrich the ethylene.

In the preferred method of carrying out dehydration by this invention, we inject ethanol at a high pressure continuously into a hot reaction zone such as a tubular reaction vessel where it comes into contact with a dehydration catalyst. With fluid catalysts the ethanol may be mixed with the catalyst and the mixture injected into the hot reaction zone. The rate of injection may be 2.20 volumes of liquid ethanol per volume of reaction zone per hour. The dehydration products are predominantly ethylene, water vapour and unchanged ethanol, but they may also contain other materials such as catalyst and by-products. When carrying out polymerisation of this crude

ethylene this mixture is passed continuously from this reaction zone through a cooler and the gas is then passed into a second reaction zone into which an aqueous solution of alkali persulphate is also injected. Both reaction zones are maintained at substantially the same pressure. The polymerisation product is withdrawn from the second reaction zone as a fused solid or as a solution or suspension in a liquid polymerisation medium, or as a liquid depending on the conditions employed.

The invention also includes the manufacture of polymerisation products containing other groups besides the recurring $-C_2H_4-$ groups, in particular interpolymers with compounds having carbon-carbon double bonds by adding such compounds after dehydration and before polymerisation.

The polymerisation products of this invention are generally solids which may be soft, waxy, or tough depending on the conditions employed. In the absence of interpolymers the polymerisation products are essentially straight or branched chain hydrocarbons composed of recurring $-C_2H_4-$ groups. In the presence of interpolymers constituents, these chains may be interrupted or terminated by other groups. When carrying out the polymerisation at the higher temperatures such as 300° – 400° C. and the lower pressures such as 50–100 atmospheres, if necessary in the presence of high proportions of polymerisation catalyst such as 1–5% by weight, the polymerisation products are liquids.

The invention is illustrated but not restricted by the following examples in which parts are by weight.

EXAMPLE 1.

A solution was made up containing 70 parts of ethanol, 10 parts of orthophosphoric acid and 20 parts of water. 100 parts of this solution were confined over mercury in a glass tube of capacity 50,000 parts of water. The tube was enclosed in a pressure vessel, a pressure of 1500 atmospheres was applied by means of hydraulic oil, and the system was heated to 310° C. for 24 hours. The temperature was then reduced to 20° , and it was found that $9\frac{1}{2}$ parts of ethylene had been formed.

EXAMPLE 2.

100 parts of a solution containing 70 parts of ethanol, 10 parts of orthophosphoric acid and 20 parts of water, were confined in a glass tube over mercury at 300° C. and 300 atmospheres pressure. Dehydration occurred, and 11 parts of ethylene were formed.

The temperature was lowered to 120° C. and $1\frac{1}{2}$ parts of benzoyl peroxide were added. After a further 20 hours at 3000 atmospheres and 120° C. the temperature and pressure were reduced to normal, and $3\frac{1}{2}$ parts of a solid ethylene polymer in the form of a chalk-like mass were collected.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the manufacture of ethylene directly under pressure which comprises subjecting ethanol to contact with a dehydration catalyst at an elevated pressure between 350 and 1500 atmospheres and a high temperature preferably 300° – 600° C. and if desired cooling and/or scrubbing the crude ethylene so obtained without considerable reduction of pressure.

2. Process as claimed in Claim 1, in which the dehydration catalyst is 1–10% of phosphoric acid based on the weight of ethanol.

3. Process as claimed in Claim 1, in which the dehydration catalyst is activated alumina.

4. Process according to Claim 1, in which the dehydration catalyst is separated from the crude ethylene.

5. Process according to Claim 2, in which the crude ethylene is treated under pressure with an aqueous solution of alkali to remove the phosphoric acid.

6. Process for the manufacture of polymerisation products having recurring $-C_2H_4-$ groups, which comprises contacting the product obtained by the process of any of the preceding claims directly with an ethylene polymerisation catalyst while still at an elevated temperature and pressure.

7. Process as claimed in Claim 6, in which the ethylene polymerisation catalyst is a per-compound, preferably a persulphate, the temperature 60° – 150° C. and the pressure 70–1000 atmospheres.

8. Process as claimed in Claim 6, in which the polymerisation catalyst is oxygen, the temperature 150° – 400° C. and the pressure above 500 atmospheres.

9. Process as claimed in any of Claims 6, 7 and 8 in which the same pressure is employed for the dehydration and polymerisation.

10. Process for the manufacture of ethylene and polymerisation products having recurring $-C_2H_4-$ groups substantially as hereinbefore described with reference to each of the foregoing examples.

11. Ethylene and polymerisation pro-

ducts having recurring $-C_2H_5-$ groups
whenever obtained by the process of any
of the preceding claims.

Dated the 3rd day of December, 1945.

E. A. BINGEN,
Solicitor for the Applicants.

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